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RELAXATION PHENOMENA IN GLASS TECHNOLOGY

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Investigations of relaxation phenomena in glasses are reviewed. The role of such phenomena in the formation and heat-treatment as well as in other technological processes is shown. The characteristics of the surface layer are indicated from the standpoint of the physics of mesomechanics and the general structural features of inorganic glasses. A number of operational reliability factors for glass articles are examined.

Key words: relaxation phenomena, structure, technological processes, formation, heat-treatment, surface layer, operational reliability.

Phenomena due to a transition from nonequilibrium to equilibrium states as a result of the displacement of kinetic units of a system are called *relaxation processes*. For this reason these phenomena are general for all processes: a system driven out of a state of equilibrium tends toward equilibrium at a rate that is proportional to the degree of departure from equilibrium.

Structural, mechanical, electric, magnetic, and other forms of relaxation are distinguished. The most widely used methods of investigating relaxation phenomena in glassy systems are thermal and mechanical, based on monitoring relaxation phenomena, including by means of relaxation spectrometry and by changing the temperature and mechanical actions applied to the objects being studied.

The most easily visualizable description of a relaxation process is the so-called temperature jump — a sharp change in the temperature of a pre-stabilized material followed by isothermal soaking at the new temperature (Fig. 1). The total change occurring in the properties in time (starting at τ_0) as a result of a temperature change $\Delta T = T_2 - T_1$ can be divided into two parts: instantaneous (isostructural) change of the properties ΔP_g and structural or relaxation change ΔP_s. An isostructural change of the properties is a result of a change in the intensity of thermal vibrations of the particles. A structural change of the properties is associated with thermally activated changes of the relative position of the particles with their vibrational intensity remaining constant.

It should be noted that relaxation phenomena unfold differently, depending on the properties, the form of the deformation, and the conditions under which relaxation occurs, and they manifest as an elastic after-effect, internal friction, and stress relaxation. A definite excess of energy must be present in the system, which is why relaxation phenomena develop. The system tends toward equilibrium only in cases where the kinetic units overcome a definite energy barrier, for example, in the presence of viscous shear (stress relaxation), or the system breaks up into individual fragments (relaxation fracture).

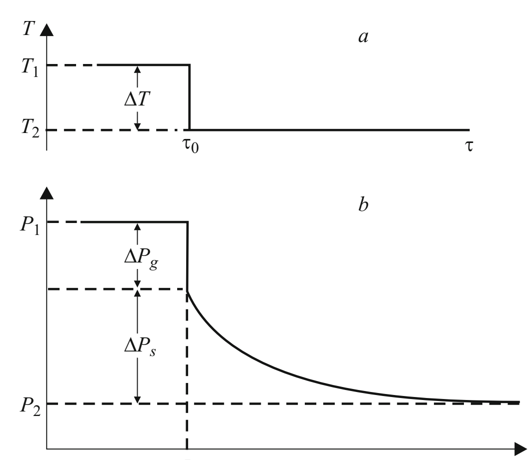

Fig. 1. General variation of the property P during the time τ as a result of a temperature jump: *a*) temperature jump; *b*) change of the property P in time during isothermal soaking.

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Glass-forming systems possess a high melt viscosity, which increases substantially during vitrification. Thus, the vitrification process exhibits a marked relaxation character.

Inorganic glasses are complex systems comprised of subsystems consisting of structural elements of different nature (atomic nuclei and electrons, ions and atoms, groups of ions, regions with short-range order, regions with microuniformity, and sections with framework-mesh glass). This results in a many different forms of mobility of the structural units and associated relaxation phenomena.

On the whole a relaxation process is multistage, consisting of individual "elementary" relaxation processes (fast and slow), each of which is related with thermal motion of definite structural elements with their own relaxation time (spectrum of relaxation times). The main results of theoretical and experimental studies of relaxation phenomena in glassy systems have been systematized and generalized in [1 – 3].

The empirical Kohlrausch function is widely used to describe relaxation phenomena in glasses:

$$\Phi_\tau = \exp\,[-(\tau/\tau^*)^b], \tag{1}$$

where $\Phi_\tau = (P_\infty - P_\tau)/(P_\infty - P_0)$ is the relaxation function for the property P; P_0 is the initial value of the property; P_∞ is the final (equilibrium) value of the property; P_τ is the value of the property at time τ; τ^* is the relaxation time; and, b is a coefficient, $0 < b \le 1$.

Relaxation phenomena occur widely in nature. The most characteristic examples are tectonic processes, which are largely due to relaxation phenomena in energy-saturated, stressed rocks in and on the surface of the Earth's crust. The effect of relaxation phenomena in and on the surface of the Earth's crust manifest over considerable time intervals, of the order of tens and hundreds of thousands of years, and have been study quite well [4]. To a certain extent these phenomena are also valid for glassy systems provided that the scale and temporal factors are taken into account.

The character of the spontaneous fracture rock in energy-saturated zones of the Earth's crust ("Simplon blocks") is similar to that of the fracture of glassy "Batavia's tears" of tempered and high-strength glass. The formation of glassy rocks (obsidians) is related with rapid cooling of volcanic lava, which is responsible for subsequent geological changes under the influence of relaxation phenomena. Likewise, the natural breakdown of ancient and middle-age glass articles is due mainly to relaxation phenomena [5].

Previous studies of the deformation of solids and the corresponding relaxation phenomena used two conventional approaches: the mechanics of continuous media (macro level) and the theory of the appearance of microdefects (micro level). Work in this direction is reviewed in detail in the monograph [6]. The kinetic nature of the strength of solids, due to the decisive role of the thermal motion of atoms in the fracture process, is also validated in [6]. In application to glass, this concept is examined in detail in the monograph [7].

The idea that the interconnected hierarchy of scales of structural levels of deformation at the micro-, meso-, and macro-levels must be taken into account when studying deformation and, correspondingly, relaxation phenomena is now being developed. A systematic study of the structural levels of deformation has led to the development of a new field in science — the physical meso-mechanics of materials. Together with volume deformation, new processes at the meso-level, which can occur only in surface layers, are being studied [8].

The most important structure-sensitive and technological property of glass is the viscosity. The viscosity of glass in technological processes is very substantial and ranges over wide limits. This is why trending toward equilibrium is much slower in glasses. An estimate of the relaxation time can be obtained on the basis of an equation presented in [1]:

$$\eta/\,\tau^* = k_r$$

or

$$\tau^* = \eta/k_r\,,$$

where η is the viscosity and k_r is a coefficient which is a constant for any given glass.

For ordinary Na – Ca – Si glasses the coefficient k_r can assume values about 10^9. In this connection, the relaxation time for viscosities $10^{10} - 10^{13}$ Pa · sec varies from tens of seconds to several hours or more.

Thus, relaxation phenomena in glasses are unavoidable in technological processes; they manifest most clearly for high values of the viscosity at the stages of formation and, especially, at the stage of subsequent heat-treatment.

A large number of works are devoted to the study of relaxation processes in glasses, especially during annealing of glass articles. The works of Russian researchers are widely known in this field. In this connection, the present author used predominately domestic reviews containing numerous references to original works, including those of foreign authors. At the same time there is not enough information in the scientific and technical literature about the role of relaxation phenomena in concrete technological processes used to obtain glass articles as well as in the use of glass articles.

Structural Aspect. In general, the structure of silicate glass is characterized by a combination of a quite rigid *silica-alumina-oxygen framework* (with a random distribution of alkali and alkali-earth metal ions) and *regions of micrononuniformities.*

Melts of silicate glasses at high temperatures maintain a spatial framework, which has an elevated mobility, including due to it lower degree of connectedness. A definite connectedness of the framework is determined primarily by the chemical bonds Si – O. More detailed information on the structure and properties (including relaxation properties) of inorganic glasses is systematized in [9].

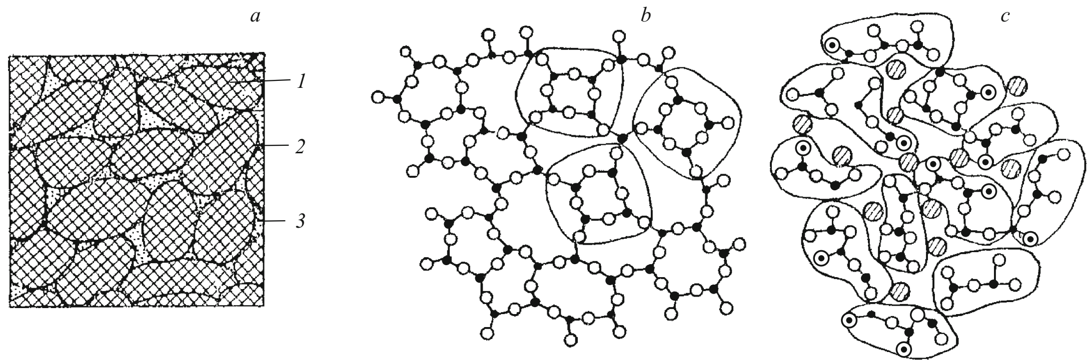

Fig. 2. Structural complexes in glass: *a*) general scheme of the structural model; *1*) structural complex; *2*) boundary regions; *3*) regions with weakened structure; *b*, *c*) structural complexes of quartz and sodium-silicate glass, respectively; ●) Si; ▨) Na; ○ and ⦿) bridge and nonbridge atomic oxygen, respectively.

Together with a spatial framework of chemical bonds there exists a spatial mesh of physical bonds, which, by analogy to organic polymers [10], can be called a fluctuation mesh. The nodes of the fluctuation mesh are regions of nonuniformity which are coupled with one another by physical bonds.

The thermal motion of the structural elements changes the fluctuation spatial mesh. Its nodes are continually decaying and reforming — they are in a state of dynamic equilibrium. The fluctuation mesh possesses a definite elasticity and resists deforming forces. The higher the deformation rate, the more the fluctuation mesh breaks down. After these forces stop acting, a certain amount of time is always required for dynamic equilibrium between the decay and restoration of the nodes of the fluctuation mesh to arise.

To study the structure of glass researchers attempted to separate its basic structural units associated with deformations and relaxation phenomena. Some approaches in this direction are reflected in [11, 12]. In particular, G. K. Demishev [11] develops, in addition to the well-known ideas about the micro-nonuniform structure of glasses underscoring the presence of chemically nonuniform regions of submicron size in their structure, the concept of heterodynamism of silicate glass, which presupposes that the mobility of separate structural elements is different.

In this case, the main structural element of the glass is a structural complex in the form of a local region of strong bonds (for example, ionic-covalent), where a definite degree of ordering is assumed to exist (Fig. 2). The structural complex interacts with similar surrounding complexes through intermediate, less ordered (or completely disordered) regions of weak and overstressed bonds. Since these and boundary regions are the weakest locations, they determine the initial stages of the behavior of glass under mechanical loads. The conditions of relaxation of the stressed structural complexes are studied.

As a result of the appearance (during vitrification, heat-treatment, or deformation of glass) of structural stresses between complexes and in the mesh of the fluctuation bonds, relaxation phenomena develop, boundary microcreep arises, and structural defects in the form of free microdefects (submicrocracks) or in the form of microregions filled with modifying complexes form. An example illustrating such a scheme is the irregular three-dimensional mesh (framework) for quartz and Na – Ca – Si glasses. In the first case the bonds between complexes are the more rare stressed Si – O bonds and in the second case they are the same bonds but with a significant fraction replaced by Na – O bonds.

The field of nano-nonuniform structure of amorphous substance and glasses has been developing in recent years [13] on the basis of studies of low-energy vibrational spectra and properties, determined by the spectral distribution of the elastic vibrations. According to models, the vibrational excitations responsible for the excess density of states in disordered bodies are localized in regions containing from several tens to hundreds of atoms and ranging in size from one to several nanometers. This attests to the presence in amorphous substances and glasses of a structure with a characteristic spatial scale, i.e., a nanostructure in these materials. In the opinion of a number of researchers, this can have just as an important role in the theory of glassy and liquid states as does the presence of a unit cell in the theory of crystal structure.

Characteristics of the Surface Layer. One feature of inorganic glasses is the difference in the structure and chemical composition between the interior volume and the surface layer. This is due to the fact that under atmospheric conditions a glass surface starts to change immediately after it is formed, and these changes bring about the formation of a thin surface layer whose chemical composition and physical – chemical properties are different from those of the rest of the glass. It is known that a film whose thickness is very small, ranging from 10 to 350 Å for different glasses, forms as a result of hydrolysis. In addition, different kinds of defects associated with the characteristics of the technological processes used in the production of glass and glass articles appear in the surface layer.

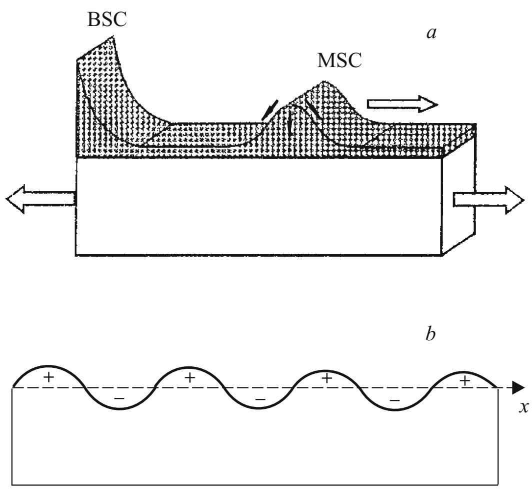

Fig. 3. Scheme of the formation of a "traveling impulse" and stress distribution in the surface layer: *a*) "traveling" impulse (BSC) base stress concentrator; MSC) microconcentrator of stress); *b*) profile of the coupling of the surface layer with the substrate (the compression and tensile stresses are indicated).

The most characteristic defects in the surface layer are microcracks due to relaxation phenomena occurring as the glass cools in different technological processes. Temperature differentials and therefore thermoelastic stresses which are especially dangerous on a glass surface unavoidably arise during the formation of glass and glass articles and during heat treatment.

The presence of different kinds of defects on a glass surface, first and foremost, microcracks, is confirmed by the fact that the strength of the glass is much greater after the surface undergoes chemical etching [2, 7, 12].

A new field direction is growing rapidly — *physical mesomechanics of materials.* The review [8] examines, on the basis of studies which have been completed, a new role for the surface layer in the deformation of solids. It is noted that the following circumstances are of fundamental importance for further development of ideas about the significance of the surface layer for the strength of solids:

the appearance of a new generation of devices which combine high resolution with scanning of extended surfaces of bodies (atomic-force and scanning tunneling microscopy, high-resolution optical-television systems, laser profilometers, and others); these devices have made it possible to reveal in the surface layers of a sample under a load not only nucleation of defects but also completely new processes at the meso- level, which can occur only in surface layers;

the development of a systems approach in physical mesomechanics, describing a deformed solid body as a multilevel system where the surface layers are an autonomous subsystem.

The excess (as compared with the interior volume) deformation of the surface layer imparts fluting to the layer and engenders a "traveling impulse" on the surface of a sample subjected to a load (Fig. 3*a*). The marked curvature in the folds that are formed is a source for the formation of stress concentrators, which generate in the surface layer deformation defects that migrate into the lower-laying layer of the material.

The character of the changes of the stress-strain state of the surface (for the case of heating of the body), which is shown schematically in Fig. 3*b*, was calculated. Evidently, the zones of compression and stretching alternate in the surface layer. The atomic-configuration redistribution pulses emitted by the base stress concentrator propagate in the surface layer in a field of maximum tangential stresses as an active relaxation process. It stops in the meso- and macrolevels. Evidently, this concept of mesomechanics can also be applied to inorganic glasses.

Character of Fracture. The character of fracture can be studied in the most general form on the basis of structural schemes (see Fig. 2). The glass can be represented as a medium that contains rigid bonds with a long relaxation time (rigid silicon-oxygen framework) and relatively weak bonds with a short relaxation time (boundary regions and regions with a weakened structure). If a load is applied to such a medium, the load becomes distributed among all bonds. With time the structural elements with a short relaxation time are the first to lose their carrying capacity, transforming into a state of microcreep. A load previously distributed over all bonds becomes concentrated on the rigid bonds. Such a redistribution of the load is equivalent to a situation where the cross section of the loaded sample gradually decreases. Ultimately, the growth of the stresses in the rigid bonds can exceed their strength and result in brittle fracture of the glass, i.e., it can become the reason for the appearance and development of cracks.

The role of relaxation phenomena in the fracture of inorganic glass was noted by G. M. Bartenev [12] for microplastic and viscoplastic fracture. The microplastic mechanism pertains to fracture of glass above the brittleness temperature (100 – 200°C) right up to the vitrification temperature. It is manifested in low-strength glasses with surface defects, first and foremost, at locations of stress concentration, for example, at the tips of microcracks. In high-strength glasses in which the defective surface layer has been removed microplastic shears are observed in weakened elements of a micro-nonuniform structure of the glass (microcreep), resulting in the formation of nuclei of microcracks and their development. Viscoplastic fracture occurring above the vitrification temperature is related with viscoplastic deformation in the volume of the sample and with instability at the weakest point.

Technological Processes. Relaxation phenomena in technological processes are manifested during the formation of glass articles and subsequent heat treatment (annealing, tempering, ion-exchange hardening, breaking off of the head in blown articles, in thermal after-effect processes, and others). The most characteristic processes associated with relaxation phenomena are examined below.

Molding of Glass Articles. During molding, together with giving articles a definite shape, a complex process of continuous solidification of glass under isothermal (thermally polished glass) and nonisothermal (hollow glass articles, glass fibers, and others) conditions occurs [14].

For definite chemical and thermal nonuniformity of the molten glass and nonuniform cooling, especially in metal molds, a "grainy" fragmentation with average grain size about 4 – 8 μm and lamination (in the transverse section of the articles) with average layer thickness about 2 – 4 μm is fixed in the glass.

Thus, the process of solidification during molding can be represented as occurring in two stages:

– appearance of "nuclei of solidification" (local regions of the glass with elevated viscosity) and formation of a "layer of solidification";

– advancement of the "layer of solidification" into the interior volume of the glass.

For high viscosity of glass-forming melts and rapid flow of the molding process, relaxation processes are unavoidable. Layerwise and nonuniform solidification greatly complicates relaxation processes, both directly during molding and during subsequent heat-treatment.

Mechanized molding of hollow glass articles (glass containers) is one of the most complex processes. Since during molding the glass surface is always being cooled more rapidly than the interior layers, it can be treated as a shell consisting of a thin viscoelastic film containing molten glass with a higher temperature. When molten glass is poured into a mold the more viscous surface film permits obtaining the required configuration of the drop. After rough molding has been completed, the surface layer hardens to such an extent that the blank formed retains its shape. The stresses arising in the process relax very rapidly. After the rough mold is opened and the blank is transferred to a finishing mold, the surface of the blank is heated once again, which makes it possible to blow the finished article. After the finishing mold is opened, the finished article retains its shape as a result of an increase of the thickness of the solidified layer, where changes due to relaxation phenomena occur.

The CLTE of glass decreases sharply (by approximately a factor of 3) in the thin solidified layer as compared with the interior layers whose viscosity is lower. As a result, quite substantial thermoelastic compression stresses appear in the surface layer, which tend to separate this layer from the lower-lying layers. Many micro- and submicro- cracks are formed in the surface layer. The freshly formed glass surfaces in the cracks immediately start to interact with the surrounding medium (first and foremost, the atmospheric moisture) with formation of gel-like products (specifically, silicic acid gel), which fill the microcracks and, to a certain extent, cement them, preventing the cracks from proliferating rapidly.

As the molded glass articles cool further, layer-wise "freezing" of the higher-temperature structure of the glass occurs because of the rapid growth of the viscosity. As a result, substantial stresses arise and there is not enough time for these stresses to relax. If conditions for relaxation of the stresses (annealing) are not created, the glass articles fracture all the more rapidly, the complex their shape and the more rapid the cool-down during molding.

When glass fiber is continually drawn out, substantial radial-thermal gradients appear between the surface and interior layers of the fiber, which results in the formation of a hardened surface layer (thickness about 0.01 – 0.02 μm) with possible structural orientation and small number of dangerous surface defects. As the same time heat-treatment of the glass fiber, for example, long-time soaking at 450°C, decreases its strength; this is explained by relaxation phenomena and the appearance of new surface defects [12].

Relaxation phenomena in glass-forming melts have been examined in [15]. Under the action of elastic oscillations on the high-viscosity glass melt, the internal parameters of the melt change; specifically, the fluctuation spatial mesh decomposes and the melt transitions from a state with viscosity η_0 into a stable "excited" state with a lower viscosity. After the elastic oscillations cease, a relaxation transition of the melt into a previous equilibrium state with viscosity η_0 is observed. The action of the elastic oscillations on glass melts depend on their structure: it is practically not reflected on $2Na_2O \cdot SiO_2$ melt and increases in the series $Na_2O \cdot SiO_2$ – $Na_2O \cdot 2SiO_2$ – $Na_2O \cdot 4SiO_2$.

An external action on a glass melt can be implemented during the molding of glass articles (pressing, casting) in order to increase the effectiveness of the process and improve the quality of the articles. Such action can be effectuated by introducing elastic oscillations in a regime with a constant deformation rate [15].

A characteristic of this regime it that the deformation rate can be higher than the decomposition rate of some nodes of the extended framework of the melt formed. These nodes can decompose under the same stresses which develop in the molten glass during the initial period. But if the deformation rate is high, then here is simply not enough time for them to decompose. As a result the stresses continue to grow, and only when the maximum value is reached does the relaxation time decrease under the action of the stresses to such an extent that there is time for the decomposition of the nodes of the framework formations to decompose for the given deformation rate. Definite decomposition of the macrostructure of the melt in such an overstressed system results in a decrease of the stresses from their maximum value to a constant value in a steady regime. In the process the viscosity of the melt decreases, thereby allowing complex molds to be filled during molding.

The viscosity changes during the molding of glass articles in molds will be fragmented on the surface (fast process) and in the interior volume (slow process) [14]. The local viscosity nonuniformities of the molten glass with rapid and continual solidification together with substantial local

stresses and the character of their variation can give rise to the appearance of foci of local decomposition of the glass, primarily in the surface and adjoining layers (“cracks”). There is time for the stresses in the interior layers of the wall of the glass article to relax to a safe level. Small surface “cracks” can appear, for example, along the edge of pressed dishware articles and along the crown of the neck of bottles and cans, since the most rapid cooling and solidification of the molten glass occurs at these locations and substantial local stresses are created there.

Annealing of glass articles after molding is entirely based on relaxation phenomena. The articles cool according to a definite regime, assuring a stress level and distribution that prevent spontaneous fracture of a glass article during use. For example, the level of attainable residual stresses is 70 nm/cm ($\sigma = 2.8$ MPa) for sheet glass and 115 nm/cm ($\sigma = 4.6$ MPa) for container glass.

The values presented for the residual stresses are completely unacceptable for optical glass [16]. Coarse and fine annealing are used for optical-glass blanks. The problem of fine annealing is to weaken the residual stresses as much as possible, attain the maximum possible structural relaxation, and impart to the glass of each blank and the entire batch the same refractive indices (with the tolerances), birefringence, and optical uniformity. In this connection, the duration of the fine annealing is very long. For example, for blanks with determining size 75 mm with the lowest annealing category with respect to optical uniformity and birefringence the annealing time is about 50 h, while for 150 mm blanks with the highest category of annealing it is about 140 h. The annealing time for large astronomical disks ranges from several months to several years.

There are a large number of studies, systematized in monographs and reviews [2, 3, 16 – 19], on questions concerning the annealing of glass and glass articles. Practical recommendations on calculating rational annealing regimes have been developed on the basis of the results of these studies. They are published in a number of works, for example [18]. Concrete examples of calculations for sheet float-glass and glass containers are presented in [20].

G. M. Bartenev and his colleagues draw conclusions about the structural character of the relaxation process in the annealing ranges of glass articles on the basis of a generalization of a series of research results, including the use of relaxation spectrometry [2, 19]. Two relaxation processes are observed at temperatures below T_g: R_1 and R_2, which are not related with equilibrium viscous flow. A relaxation process R_3, responsible for viscous flow, is practically not observed because the velocity is low in the annealing region, with the exception of temperatures close to T_g. The processes R_1 and R_2 are related with the mobility of large kinetic units, while the process R_3 is related with the mobility of small kinetic units (silicon and oxygen ions). It supposed that the relaxation process R_1 is related with local deformations of the fluctuation mesh of the glass, while the process R_2 is related with the mobility of microregions of the nonuniform structure of the glass (structural complexes, microblocks). Studies of the relaxation characteristics of alkali glass (sheet, container, and others) and low-alkali glass have established that the contribution of the process R_2 to stress relaxation during annealing is about 70 and 80%, respectively, while the contribution of the R_3 process is only about 5%.

Tempering of Glass Articles. During tempering substantial internal stresses are obtained in glass by rapidly cooling the glass from temperatures above the vitrification temperature. The tempered glass is characterized by the presence of substantial stresses distributed over the volume in a way so that compression stresses are created in the outer layers and tensile stresses in the inner layers. Such a stress distribution is due to nonuniform cooling of the glass from the tempering temperature, which is above T_g for a given glass [17, 18, 21].

Compared with annealed glass, tempered glass is much farther from equilibrium and energy-saturated, as a result of which annealed glass undergoes relaxation fracture into fine fragments. According to experimental data [21], the neutral layer in glasses with different degrees of tempering is found at a distance from the surface 0.35 – 0.40 times the half-thickness of the glass. Thus, the most dangerous tensile stresses act in the largest part of the glass volume and are found in a comparatively thin “shell” of higher compression stresses. For this reason when this “shell” is damaged the tensile stresses emerge on the surface of the glass and are the reason for the fine-fragmentary form of the fracture of the glass.

There are substantial number of works on the investigation of the tempering process in glasses and its practical application. Many of these works are systematized in [21]. In this work I. A. Boguslavskii gives relations showing that the thinner the glass and the more intense the tempering, the larger the increase in strength as compared with the expected value is. The author attributes these results to the microplastic state of the glass surface, associated with the high intensity of tempering. In a review article [22], F. M. Ernsberger notes that under certain conditions glass can be stable with respect to the effect of surface cracks in a manner similar to metals, so that further investigations in this direction will be helpful. In this connection, I. A. Boguslavskii’s [21] can be now be studied in the light of the concept of physical mesomechanics, developed in [8].

The most favorable conditions for heat transfer and tempering obtain for articles made of sheet glass owing to their flat shape. The conditions for tempering become much more complicated in the production of hollow tempered dishware, for example, pressed drinking glasses with decorative designs. The nonuniform thickness of the walls and bottom degrades heat transfer and makes quenching less effective.

The conditions for tempering of glass insulators are even more complicated; together with their complex shape these articles are quite thick. In this connection the articles are characterized by definite nonuniformity of the distribution of tempering stresses. Glass insulators are used under unfavor-

able climatic conditions with quite large temperature and load variations. After quenching all articles are subjected to quite rigorous heat tests:

– positive thermal shock in a heat-control furnace with temperature differential 300°C; the tempering stresses are normalized as a result of partial relaxation, especially in the overstressed sections of the articles; a temporary increase of the compression stresses occurs in the surface layer as a result of thermoelastic stresses, which results in fracture of articles in which there is a potential possibility of spontaneous fracture, caused by, for example, small foreign inclusions in the glass;

– negative heat shock in a cold-water bath with temperature differential 120°C; temporary thermoelastic stresses arise in the surface layer, which results in activation of relaxation – thermal fluctuation fracture of articles containing locations with weak, nonuniform tempering or the presence on the surface of potentially dangerous defects (“cracks”);

– positive heat shock in a hot-water bath with temperature differential 70°C; the thermoelastic compressive stresses arising normalize the state of the surface of glass insulators.

Articles with defects are rejected in the course of heat tests. This makes it possible to guarantee that the heat insulators have the prescribed characteristics.

It should be noted that relaxation of temper stresses, which is activated with an increase of temperature, proceeds very slowly in tempered articles. Thus, stress relaxation in tempered glasses plays a negative role, the operational reliability of tempered articles decreases since with time (though quite long time) and especially at elevated temperatures.

Ion-Exchange Hardening. The low-temperature method is associated with replacement in the surface layer of the glass of a small alkali ion by a larger alkali ion from an external source at temperature below T_g. During treatment of the surface of a glass containing sodium ions in a potassium nitrate melt, compression stresses arise as a result of an ion-exchange reaction:

$$(\equiv \mathrm{Si} - \mathrm{O}^- - \mathrm{Na}^+) + \mathrm{K}^+ \rightleftarrows (\equiv \mathrm{Si} - \mathrm{O}^- - \mathrm{K}^+) + \mathrm{Na}^+.$$

Ion-exchange compression stresses, in contrast to tempering stresses, are distributed in a thin surface layer and are 3 – 4 times higher than tempering stresses together with much lower central tensile stresses, which eliminate spontaneous fracture of articles during storage and mechanical working. The indisputable advantages of ion-exchange technology appear during hardening of thin glasses and glass articles with a complicated configuration, including hollow articles and articles with variable thickness. Even though ion-exchange hardening has obvious advantages, the drawbacks should also be noted: the effect of the composition on the degree of hardening and high sensitivity of the hardened glass to abrasion. Ion-exchange hardening is investigated in a considerable number of works, which are systematized in [23].

The relaxation of ion-exchange stresses occurs in a thin layer and is due to the redistribution of the alkali ions A^+ and B^+ in a modified layer and to the mobility of small kinetic units which are responsible for viscous flow. In [3] relaxation is regarded as a structural rearrangement of the glass framework adapted to the exchange of the alkali ions A^+ and B^+. In [23] attention is drawn to the fact that the character of the relaxation of stresses on the surface is different from that in the interior volume of the glass. Annealing can change even the sign of the stresses on the surface without changing the absolute value of the residual stresses beneath the surface layer. The concept of physical mesomechanics [8] briefly expounded above can be examined in this connection.

The relaxation of ion-exchange stresses is related with the thermal stability of the strength, which increases as the state of the glass surface improves and the ion exchange time and the difference of the radii of the exchanged ions increases. For example, lithium-aluminum-silicate glass hardened by the exchange of ions $\mathrm{Li}^+ \rightleftarrows \mathrm{K}^+$ with soaking at 400°C in air did not lose its initial strength [23].

Combined Methods of Hardening. These methods are quite widely elucidated in the scientific and patent literature [21 – 23]. However, only the so-called thermophysical method which combines tempering and etching [21] and the methods combining ion exchange with etching and tempering [23] have been implemented physically in practice adequately. In these cases there is a possibility of compensating (though only partially) the drawbacks inherent in each of them. The first method is expected to yield a high-strength material and the second one a glass with a compressed layer with substantial thickness.

Thermal Contact Compounds. This group includes technological processes associated with the deposition of various coatings, obtaining articles with superimposed glass, articles welded with metal, ceramic, and so forth. In this case, the main property characterizing the nonequilibrium nature and relaxation level of the system is the CLTE — more accurately, the difference of the CLTEs of the materials being joined. The larger this difference, the larger the thermal-contact stresses arising in the finished articles are. When an admissible stress level is exceeded, not only does the operational reliability decrease but the article or a part of it fractures [24, 25].

When a thin layer of silicate paints is deposited on a glass article and the CLTE of the glass differs considerably from that of the paint, high stresses appear and the coating undergoes relaxation fracture. The character of crack formation in a layer of paint is similar to that of the formation of microcracks in a thin surface layer of glass articles during their formation and to the character of the surface fracture of rocks.

Solid inclusions in molten glass, for example, the products of decomposition of the refractories of a glassmaking furnace create high local stresses in articles. These stresses, likewise due the difference between the CLTE of glass and that of the inclusions, are not eliminated during annealing

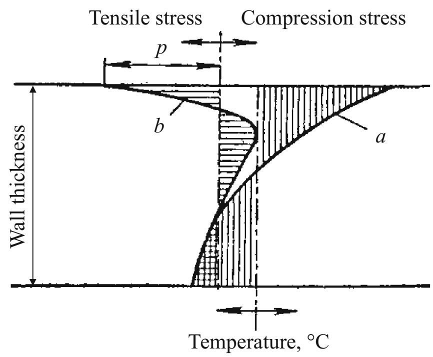

Fig. 4. Stress distribution in the wall of an article as a result of unilateral heating.

and decrease strength, and they can cause articles to fracture [24].

More complicated problems must be solved during heat-contact joining of glass and metals [25]. Thermal contact stresses in such joints cannot be avoided not only because it is impossible to match the CLTE of the materials being joined but also because of the better thermal conductivity of metal, which creates a nonuniform temperature and relaxation "zonality." Thermal contact stresses can be decreased by choosing appropriate chemical compositions of the glasses, using powders and transitional glasses, a special design of the metal parts, and so on. In addition, the heat-treatment regime (annealing) after thermal-contact joining plays a special role — annealing greatly decreases stresses as a result of relaxation or creates the optimal and safe stress distribution. For example, differentiated annealing is used for unmatched connections [25].

Splitting-off the Heads of Blown Articles. This operation of the technological cycle is based on directed thermal action (heating – cooling) on a narrow section of the surface of an article and the creation, as a result of this, of high temporary thermoelastic stresses, exceeding the maximum strength of the glass and resulting in its relaxation – thermal-fluctuation fracture (formation of a through crack on the section required), in the glass.

The appearance of stresses during thermal action is primarily due to low thermal conductivity of the glass. The following phenomena occur as a result:

large temperature gradients appear during heating and cooling;

the volumes and dimensions of the sections of the glass articles being heated and cooled change nonuniformly.

A diagram of the stress and temperature distributions in the wall of an article with unilateral heating is presented in Fig. 4.

Under rapid unilateral heating of the exterior side of the wall of an article compression stresses which decrease over the thickness of the wall arise in the surface layers of the article (see Fig. 4, curve a). The equilibrium compression and tensile stresses are characterized by equal areas relative to the vertical dashed line for the curve a. Stresses due to the temperature gradients over the thickness of the wall and over both sides from the heating zone arise as a result of rapid unilateral heating of a narrow surface zone of an article. The compression stresses arise on the exterior side of the wall of the article and tensile stresses arise on the interior side.

If the narrow heated section of the wall of an article cools rapidly from the exterior side, then the sign of the stresses changes, the section is subject to unloading, and the distribution of the stresses over the thickness of the wall of the article will take the form of curve b (see Fig. 4). If a vertical dashed line forming equal areas for compression and tensile stresses is also drawn here, then it becomes evident that high tensile stresses (of magnitude p) arise on the exterior side of the wall of the article. Tensile stresses also arise on the interior side of the wall, but they are lower than on the exterior side, where they exceed the ultimate strength of the glass. This results in the formation of a surface crack which propagates rapidly only the thickness of the wall and the perimeter of the article. To accelerate the process the exterior surface of the article is cut with a diamond, where required, before heating; the cut is a stress concentrator. In this case cracking starts when the heated section leaves the heating zone as a result of its being cooled by the surrounding air. Heating of the wall of an article without precutting can be used, but then a cold metal or abrasive sharpened rod must be touched to the surface of the heated zone along the separation line of the head. This method is usually used in mechanized production of blown articles. However, in this case the quality of the break-off decreases.

The technological aspects of manual break-off of the heads of blown articles are examined in [26]. We have obtained similar results in work performed at the Gusev' Crystal Glass and Experimental Glass Works. It was established that at the moment a crack appears the thickness of the interior wall of the article always reaches 150 – 200°C irrespective of the temperature of the exterior surface of the article. On the basis of an analysis of the experimental data and taking account of the assumptions stated in [6, 7] we suppose that the high rate of fracturing of glass in this temperature interval is probably due to activation of thermal diffusion processes and physical-chemical changes occurring in the surface layer on heating (removal of the condensed, adsorbed, and partially structure-associated moisture). In the process, the surface becomes "embrittled" and "shrinks," as a result of which tensile stresses arise in it, lower the strength, and cause the glass to fracture. This is confirmed by the result of experiments with water-filled articles [26]. When a narrow zone of the article below the water level was heated, cracking did not occur even in the case where the surface was cut with a diamond. In the case where the flames from burners were placed in the plane of the water level, a head was broken off only when the part of the water that cooled the section along the separation line of the head evaporated, and this section was heated to critical temperatures (150 – 200°C).

Operational Characteristics of Glasses and Relaxation Phenomena. Glass article are used under various conditions. Relaxation phenomena must be taken into account for many articles. This concerns, first and foremost, articles strengthened by tempering and ion-exchange. The relaxation phenomena play an important role during long-time use of articles made of thermometric, optical, and other types of glass (aging). These phenomena must also be taken into account during exposure to radiation and for thermal and optical methods of destroying induced-color centers.

Strength is the most important characteristic of glass and glass articles and predominately determines the operational reliability of most massive forms of glass. There are many studies devoted to the theoretical and practical aspects of strength; these studies are generalized in [7, 12, 21 – 24]. Taking into account modern requirements for buildings, structures, and technical constructs, glass articles must be regarded not only as an enclosing material that transmits light but also as a construction material which is supposed to withstand prolonged mechanical loads [12, 21, 22, 23, 27, 28].

This is especially true for glass articles used for long periods of time at elevated temperatures. In this case the tempering and ion-exchange stresses relax and micro-creep phenomena develop. The time required for stresses to decrease, as a result of relaxation, and the operational reliability to decrease ranges over very side limits — from many tens and even hundreds of years at room temperature to several seconds at temperatures of the order of 500 – 600°C.

There is no “critical temperature,” separating the stable state from a state facilitating stress relaxation, between these extreme limits. There are relaxation diagrams which make it possible to determine the highest admissible temperature of the surrounding medium, depending on the required service life of the glass article and the minimum admissible stress level. The following example of the use of relaxation diagrams is presented in [22]: if the glass article is to last for one year and the minimum tensile stress is 800 nm/cm (32 MPa), then the maximum working temperature is about 325°C.

It should be noted that glass is used as a construction material — glazing of space vehicles and airplanes. Very high requirements on imposed on such glazing elements. They must possess high strength and reliability, resistance to aerodynamic heating, good optical properties, and a mass which is as small as possible, and they must ensure safe completion of the flight under unfavorable conditions.

In modern space vehicles, glass articles function not only as optical elements but also as a construction material, capable of withstanding various types of loads and making the vehicle reliable as a whole and the crew safe.

For example, the portholes of re-usable space ships consist of three panels. The first and middle panels (thermal) are made of optical quartz glass; the interior panel (pressure) is made of strengthened glass. The cockpit glass of jet airplanes also has a layered structure, for example, consisting of thermally and chemically stable glass, two polyvinyl butaryl layers and two tempered glasses. Ion-exchange strengthened glass is also used [23].

A method of predicting on the basis of previous work the longevity of glass articles under prolonged variable loads is also presented in [27]. The operational reliability of various types of glass articles and the character of their fracture are also examined in [21 – 24, 27 – 29].

Physical Aging of Silicate Glasses. These phenomena must be taken into account in the manufacture and usage of a number of glass articles. They are most characteristic for articles made of thermometric glass (thermometers) and manifest as natural aging (positive displacement of the zero point) and thermal after-effects — depression (negative displacement of the zero point).

Aging — this is a natural process where the volume of the reservoir and capillary of a thermometer decrease slowly from the moment it is manufactured. This process is due to structural relaxation phenomena associated with a change of the properties of glass, specifically, with a density increase. As glass ages, the thermometer’s temperature indications systematically increase, depending on the temperature being measured and the length of time for which the thermometer has been in use. The volumes of the reservoir and the capillary change gradually, over the entire period of storage and operation of the thermometer, along a curve which is characteristic for relaxation phenomena.

The aging of glass and the associated slow decrease of the volume of the manufactured articles also change the length of glass scales placed on automatic detailing stands and therefore the work is less accurate. For the same reason the operation of optical measuring instruments and large-size optical systems is disrupted because of changes of the radii of curvature of lenses with time. Aging of glass in instruments can cause disruptions in the operation of delay lines for acoustic signals, and so on.

Depression — this is a temporary residual expansion of a thermometer’s reservoir and capillary, which starts after the glass parts of the thermometer are heated and rapidly cooled. Rapid cooling of the thermometer to the melting point of ice after prolonged heating at the boiling point of water results in (as a result of depression) a deviation of no more than 0.05°C in the temperature indications. After heating at higher temperatures a depression can cause substantial deviation of the temperature.

To eliminate these phenomena articles to be used for thermometric purposes are manufactured from heat-resistant glass and aged artificially. This process is similar to annealing, but it is of longer duration and is conducted at a higher temperature, for example, articles are soaked at 500°C for 10 h. Relaxation stabilization of the structure [1 – 3], which has its own characteristic features, occurs in the process [30].

The diagram of aging and thermal after-effects [30] is presented in Fig. 5. The figure also displays the time variation of the indications of the thermometer, whence it is evident that artificial aging decreases the magnitude of the positive shift of the zero point.

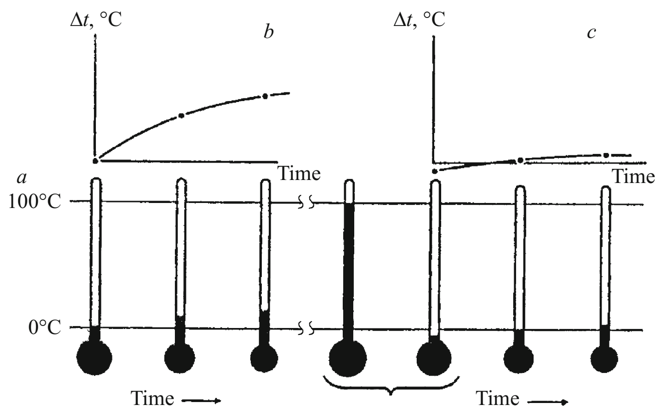

Fig. 5. Aging and thermal after-effect in thermometric glass articles: *a*) general scheme; *b*) time-dependence of the rise of the zero point of a thermometer; *c*) effect of artificial aging of thermometric glass articles on the depression of the zero point.

S. V. Nemilov has made a deep scientific analysis of the aging of glass [30], using, among other things, little-known data obtained at the end of the 19th and beginning of 20th centuries. The longest observation time in these works was 38 yr. To perform a mathematical analysis the Kohlrausch function (1) was used to fit the time variations of the properties. Relations characterizing the aging process in glasses were obtained. A theoretical validation of the aging process, presuming that cooperative β-relaxation processes which do not include α-relaxation (viscous shear) occur, is proposed.

Effect of Radiation on Glass. Irradiation of glass with ionizing high-energy radiation (x-rays, γ-rays, neutrons) disrupts the equilibrium in the atomic-electron subsystem, which transitions into an excited state characterized by the appearance of induced color. Definite changes occur in the structure of glasses. Ultraviolet radiation also falls into this group but its effect is weaker. Experimental data show that relaxation phenomena are responsible for the subsystem returning to the equilibrium state and for weakening and vanishing of color [31, 32].

Thermal and *optical* stimulation are the most active factors which destroy radiation-induced color centers. In the first case this is due to the heating of colored glass, and in the second to irradiation with light whose photons have a definite energy.

Solarization — the appearance of color tone in colorless glass containing impurities of variable-valence elements with prolonged exposure to solar radiation (UV radiation). Classic solarization is due to a change of the valence of manganese ions, which up to the mid-1900s were used to decolorize glass. In the process of solarization photochemical interactions occur in accordance with the reaction

$$Mn^{2+} + h\nu \rightarrow Mn^{3+} + e^{w},$$

where $h\nu$ is the photon energy and e^{w} is an excited electron.

Glass acquires a rose tone. Solarization can also occur if cerium and arsenic ions are present in the glass simultaneously:

$$2Ce^{3+} + As^{5+} + h\nu \rightarrow 2Ce^{4+} + As^{3+}.$$

In this case the glass acquires yellow and brown tones. Solarization of glasses containing cerium oxide is intensified when TiO_2 is present in the glass. The after-effects of solarization are eliminated by heating to 400 – 500°C.

Uviol glass ages when it is exposed to UV radiation for a long period of time. The degree of oxidation of iron changes: $Fe^{3+} + h\nu \rightarrow Fe^{3+} + e^{w}$. In this case Fe^{3+} has a wide absorption band in the near-UV region of the spectrum, which is why UV transmission of the glass decreases. Even though uviol glass contains very small quantities of iron compounds, these compounds have a very large effect with constant exposure to UV radiation. Heat-treatment can eliminate the consequences of aging of uviol glass.

Photochromic glass. A distinguishing feature of photochromic glass is repeated reversible change of the light transmission under cyclic exposure to active UV radiation. At the moment of exposure to active UV radiation photochromic glass gradually darkens; the optical density reaches its maximum value 1 – 2 min after exposure to UV radiation starts. After exposure ends the color becomes weaker and vanishes as a result of relaxation.

Glass colored by the action of high-energy radiation. High-energy ionizing radiation (x-rays, neutrons, γ-rays) breaks chemical bonds, partially displaces atoms, forms valence unsaturated coordination groupings and, in consequence, produces a number of structural defects. Free electrons and "holes," which can be trapped by structural defects and form color centers which are free to absorb visible-range radiation, are formed. The absorption spectrum is complex; brown tones due to the superposition of bands from different color centers predominate in it.

For silicate glasses the main process destroying radiation-induced color centers is relaxation change of the structure and recombination of electrons freed from "traps" by means of thermal or optical stimulation [32].

The information presented above shows that relaxation phenomena play an important role in the technology of glass and in the usage of glass articles. In this connection, further studies of relaxation phenomena in glasses are needed to increase the efficiency of technological processes and the reliability of glass articles.

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